



# Atoms, entropy, quanta: Einstein's miraculous argument of 1905

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## Abstract

In the sixth section of his light quantum paper of 1905, Einstein presented the miraculous argument, as I shall call it. Pointing out an analogy with ideal gases and dilute solutions, he showed that the macroscopic, thermodynamic properties of high-frequency heat radiation carry a distinctive signature of finitely many, spatially localized, independent components and so inferred that it consists of quanta. I describe how Einstein's other statistical papers of 1905 had already developed and exploited the idea that the ideal gas law is another macroscopic signature of finitely many, spatially localized, independent components and that these papers in turn drew on his first two, "worthless" papers of 1901 and 1902 on intermolecular forces. However, while the ideal gas law was a secure signature of independence, it was harder to use as an indicator that there are finitely many components and that they are spatially localized. Further, since his analysis of the ideal gas law depended on the assumption that the number of components was fixed, its use was precluded for heat radiation, whose component quanta vary in number in most processes. So Einstein needed and found another, more powerful signature of discreteness applicable to heat radiation and which indicated all these properties. It used one of the few processes, volume fluctuation, in which heat radiation does not alter the number of quanta.

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## 1. Introduction

In a mildly worded series of papers in the *Annalen der Physik* of 1905,<sup>1</sup> Einstein established the reality of atoms, announced special relativity and the inertia of energy and

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<sup>1</sup>Translations of text from these papers are from [Stachel \(1998\)](#).

proposed the light quantum. These works of his *annus mirabilis*, his year of miracles, contain many memorable moments. In the first sections of the special relativity paper (Einstein, 1905d), Einstein sketched a simple procedure for using light signals to synchronize clocks. From it, Einstein coaxed forth the relativity of simultaneity and, from that, the compatibility of the principle of relativity and the constancy of the speed of light of Maxwell's electrodynamics. In his (Einstein, 1905e), Einstein imagined a body symmetrically emitting electromagnetic radiation and, from that simple arrangement, inferred that every unit of energy  $E$  carries a mass  $m$  according to the formula,  $E = mc^2$ .

Yet nothing in these papers quite matches the audacity of the light quantum paper (Einstein, 1905a), the first paper published in the series. Both special relativity and the inertia of energy constitute a fulfillment of the 19th century tradition in electrodynamics, an expression of results that somehow were already in the perfected electrodynamics and were just awaiting an Einstein to find them. The light quantum paper is quite different. Its basic proposal—that light sometimes behaves as if it consisted of independent, spatially localized quanta of energy—stands in direct contradiction with that most perfect product of 19th century science. No doubt that is why Einstein chose to single out this paper alone among the works of 1905 as “very revolutionary” in his famous letter of May 1905 to his friend Conrad Habicht (Papers, Vol. 5, Doc. 27).<sup>2</sup>

The master stroke of that paper comes in its sixth section. Einstein takes what looks like a dreary fragment of the thermodynamics of heat radiation, an empirically based expression for the entropy of a volume of high-frequency heat radiation. In a few deft inferences he converts this expression into a simple, probabilistic formula whose unavoidable interpretation is that the energy of radiation is spatially localized in finitely many, independent points. We are startled, wondering what happened to the waves of light of the 19th century theory and marveling at how Einstein could see the signature of atomic discreteness in the bland formulae of thermodynamics. This inference is Einstein's miraculous argument, as I shall call it here.

It is easy to imagine that the strategy of this argument is without precedent. For here is Einstein inferring *from* the empirically determined macroproperties of heat radiation *to* its microstructure. The more usual inference proceeds in the opposite direction. We tend to think of the microstructure as something hidden and inaccessible; we must hypothesize or conjecture it and then from that supposition infer empirically testable macroproperties that no longer bear any obvious imprint of the microstructure. The sense of novelty of Einstein's strategy is heightened by the company his argument keeps. It comes in a paper whose principle theses are without precedent. It is the first paper of the new century that unequivocally argues that classical physics is unable to treat the phenomena of heat radiation adequately<sup>3</sup>; and it urges that we must tamper with the wave character of light, one of the foundational results of 19th century physics.

My purpose in this paper is to describe how Einstein's strategy in this miraculous argument did have an important precedent and one that was integrated into his other work of 1905.<sup>4</sup> That a thermal system conforms to the ideal gas law is the signature of a

<sup>2</sup>Klein et al. (Eds.) (1993).

<sup>3</sup>A casual reader of Planck's papers of 1900, innocent of what is to come, would have no real inkling that they are beginning to pull the thread that will unravel classical physics—a fact correctly emphasized by Kuhn (1978).

<sup>4</sup>Irons (2004) also stresses the connection of Einstein's miraculous argument with the statistical physics of gases, but suggests that a circularity may enter the argument with Einstein's presumption of particle like volume fluctuations for radiation. For a general view of Einstein's statistical papers of 1905, see the editorial headnotes of Stachel et al. (1989) and, for recent scholarship, Howard and Stachel (2000) and Uffink (2006).

particular microstructure: the system consists of finitely many, spatially localized, independent components. This idea had become part of the standard repertoire of Einstein's statistical physics of 1905. His statistical papers of 1905—his doctoral dissertation (Einstein, 1905b) and his Brownian motion paper (Einstein, 1905c)—used it for ideal gases, dilute solutions and suspensions; and the Brownian motion paper contained a quite serviceable demonstration of the result. What Einstein did not mention in these papers of 1905 was that he was well prepared to deal with the macroscopic manifestations of the independence of microscopic components. For that was just the simplest case of the problem he had dealt with at length in his first two publications (Einstein, 1901, 1902a). There he had sought empirical evidence for a particular law for intermolecular forces in the phenomena of capillarity and electrolysis. Independence is just the simplest case of no intermolecular forces. One theoretical device, introduced casually into the work of 1905, had been developed with much greater caution in his work of 1902. It was the notion that one could equilibrate the osmotic pressure of solutes (or partial pressure of gas components) with external conservative forces and thereby gain easy theoretical access to the average tendency of molecules to scatter under their random thermal motions.

So the recognition in the light quantum paper of the signature of finitely many, spatially localized, independent components in the macroscopic properties of heat radiation is a natural extension of what was already in Einstein's work on molecular reality and Brownian motion. The result is astonishing; the approach and method is not.

However, I will also argue that Einstein's use of this signature in the case of heat radiation presented a novel challenge. For the ideal gas law was a good signature for the independence of components, but harder to use without circularity as an indicator of their finite number and spatial localization. Also, the methods that Einstein used in his statistical papers for ideal gases, dilute solutions and suspensions were based on the assumption that these systems had fixed numbers of components. That assumption failed if the components were the quanta of heat radiation, for these quanta can be created by as simple a process as an isothermal expansion. Einstein's real innovation in his miraculous argument were these. He discovered a new signature for this same microscopic fact that could be used for thermal systems with variable numbers of components. His new signature made much more transparent that the components are spatially localized and finite in number. And he had the nerve to apply it in a domain in which it gave results that challenged the greatest success of the physics of his age.

The most important perspective this study offers is that we should not just think of the light quantum paper as a contribution to electrodynamics, where it represents an entirely novel turn. Rather, it is a natural, but inspired, development of Einstein's program of research in statistical physics that extends back at least to his early papers of 1901 and 1902. That program is dominated by the same question that governs the light quantum paper: how are the microscopic properties of matter manifested in their macroscopic thermodynamics properties, and, especially, how is the independence of the microscopic components expressed?

In the following section, I will review how the ideal gas law serves as the macroscopic signature of a microstructure of finitely many, spatially localized, independent components and indicate how this notion had entered into the statistical physics of Einstein's time. Its

argument will be developed in a more precise form in the Appendix. In the third section of this paper, I will sketch the relevant parts of Einstein's other statistical papers of 1905 and the preparation for this work in his papers of 1901 and 1902. The fourth section will recount the miraculous argument as it appears in Einstein's light quantum paper. In the fifth section, I will review the close similarity between the statistical physics of ideal gases, dilute solutions and light quanta, noting that they all obey the ideal gas law; and I will note the implications of the key dissimilarity: the number of quanta is variable, whereas the number of molecules is fixed.

In recounting the commonalities among the Einstein's statistical papers of 1905 I will assume that Einstein had grasped the essential statistical physics of ideal gases and other systems of independent components before he developed the miraculous argument of the light quantum paper. This is the natural logical development of the ideas and reflected in the order of presentation of the papers in [Stachel \(1998\)](#), which presents the light quantum paper last. It contradicts the order of publication of the three papers. The dissertation is dated April 30, 1905; the Brownian motion paper was received May 11, 1905; and the light quantum paper was received March 17, 1905. Not so much should be read into this order of publication since these dates are only weeks apart. The timing is further compressed by a cross-reference in the dissertation to the later Brownian motion paper, indicating that its content was already known to Einstein at the time of the writing of the dissertation. The strongest reason for dating the miraculous argument of the light quantum paper last, however, is that Einstein's papers of 1901 and 1902 already contain key elements of his 1905 analysis of ideal gases and dilute solutions.

Finally, by "signature," I intend to convey the notion that the inference from the macroscopic signature to the microscopic properties is an inductive inference, but an especially secure one. While it is conceivable that systems of non-localized, interacting components could somehow be contrived so that they still manifest the relevant signature, the dependency of entropy on the logarithm of volume, Einstein clearly thought this unlikely.

## **2. The macroscopic signature of atomism**

For a century and a half, it has been traditional to introduce the ideal gas law by tracing out in some detail the pressure resulting from collisions of individual molecules of a gas with the walls of a containing vessel. This sort of derivation fosters the misapprehension that the ideal gas law requires the detailed ontology of an ideal gas: tiny molecules, largely moving uniformly in straight lines and only rarely interacting with other molecules. Thus, it is puzzling when one first hears that the osmotic pressure of a dilute solution obeys this same law. The molecules of solutes, even in dilute solution, are not moving uniformly in straight lines but entering into complicated interactions with pervasive solvent molecules. So, we wonder, why should their osmotic pressure conform to the law that governs ideal gases?

The reason that both dilute solutions and ideal gases conform to the same law is that their microstructures agree in the one aspect only that is needed to assure the ideal gas law: they are both thermal systems consisting of finitely many, spatially localized, independent components.

2.1. *The simple argument*

A simple argument lets us see this fact. Consider a system consisting of finitely many, spatially localized, independent components, such as an ideal gas or solute in dilute solution, located in a gravitational field. The probability that a component is positioned at height  $h$  in the gravitational field is, according to the Maxwell-Boltzmann distribution, proportional to

$$\exp(-E(h)/kT) \tag{1}$$

where  $E(h)$  is the gravitational energy of the component at height  $h$  and  $k$  is Boltzmann’s constant. The localization in space of components is expressed by the fact that the energy depends upon a single position coordinate in space. The independence of the components is expressed by the absence of interaction energies in this factor (1); the energy of a component is simply fixed by its height, not its position relative to other components.

It now follows that the density  $\rho(h)$  at height  $h$  of components is given by

$$\rho(h) = \rho(0) \exp(-E(h)/kT),$$

where we set  $E(0) = 0$  by convention. The density gradient is recovered by differentiation

$$d\rho(h)/dh = -(1/kT)(dE(h)/dh)\rho(h).$$

The gravitational force density  $f(h)$  is just

$$f(h) = -(dE(h)/dh)\rho(h),$$

and it is balanced by a gradient in the pressure  $P$  for which

$$f(h) = dP(h)/dh.$$

Combining the last three equations we have

$$(d/dh)(P - \rho kT) = 0.$$

Assuming  $P$  vanishes for vanishing  $\rho$ , its solution is

$$P = \rho kT. \tag{2}$$

It is equivalent to the usual expression for the ideal gas law for the case of a gravitation free system of  $n$  components of uniform density spread over volume  $V$  in which  $\rho = n/V$ , so that

$$PV = nkT. \tag{3}$$

The important point to note is what is not in the derivation. There is nothing about a gas with molecules moving freely in straight lines between infrequent collisions.<sup>5</sup> As a result, the derivation works for many other systems such as: a component gas or vapor in a gas mixture; a solute exerting osmotic pressure in a dilute solutions; and larger, microscopically visible particles suspended in a liquid.

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<sup>5</sup>Of course gravitation plays only an indirect role in the argument as a probe of this factor, so the overall result is independent of gravitation. Other probes give the same result.

## 2.2. *What constitutes discreteness*

This derivation is sufficiently direct for it to be plausible that it can be reversed, so that we may proceed from the ideal gas law back at least to the initial assumption of independence of components. Of course the details of the inference in both directions are a little more complicated, so a slightly more careful version of the forward and reversed arguments is laid out in the Appendix. This use of the ideal gas law to indicate the microscopic constitution of the system is its use as what I call its use as a signature of discreteness. The inference is usually inductive, although these inferences can often be made deductive by supplementing them with further assumptions, as I show in the appendix.

The properties of the system used to deduce the ideal gas law and which constitute the discreteness of the system, are given below, along with how each property is expressed in the system's phase space:

Physical property	Expression in phase space
A. <i>Finitely many components.</i> The system consists of finitely many components.	A'. The system's phase space is finite dimensioned.
B. <i>Spatial localization.</i> The individual components are localized to one point in space.	B'. The spatial properties of each component are represented by a single position in space in the system's Hamiltonian, that is, by three, canonical, spatial coordinates of the system's phase space.
C. <i>Independence.</i> The individual components do not interact.	C'. There are no interaction energy terms in the system's Hamiltonian.

The physical properties and the corresponding expressions in the phase space are equivalent, excepting anomalous systems. The most likely breakdown of equivalence is in B. We may, as does Einstein in his Brownian motion paper (Section 3.2), represent spatially extended bodies by the spatial position of their centers of mass. However, in so far as the extension of these bodies plays no role in their dynamics, these bodies will behave like spatially localized point masses. If the extensions of the bodies is to affect the dynamics, then the extensions must be expressed somehow in the system's Hamiltonian, through some sort of size parameter. For example, at high densities, spatially extended components may resist compression when their perimeters approach, contributing a van der Waal's term to the gas law. This effect is precluded by the assumption of B' that the spatial properties of each component is represented just by a single position in space; there are no quantities in the Hamiltonian corresponding to the size of the components.

As to the use of the ideal gas law as a signature, the "Macro to Micro" inferences of the Appendix indicate how we can proceed from the macroscopic fact of the ideal gas law to C, Independence. These inferences do not preclude interactions via the momentum degrees of freedom, that is, interaction energies that are a function only of the canonical momenta. If we are to preclude such interactions, it must be through other considerations.

Since these interactions would not be diluted by distance, each component would interact equally with all others. Therefore, the local properties of the system would vary with the size of the whole system and divergences would threaten in the limit of infinitely large systems.

Inferring back further to *A*, Finitely many components, and *B*, Spatial localization, is more difficult and may be circular according to what we take the macroscopic result to be. The extended macroscopic expression of the ideal gas law— $PV = nkT$ —already assumes that we know that there are finitely many components  $n$ , so it presumes *A*. The local form of the ideal gas law— $P = \rho kT$ —presumes *B*, Spatial localization, in that the component density,  $\rho = \lim_{V \rightarrow 0} n/V$ , is defined at a point for a non-uniform component distribution. The existence of the limit entails that the number of components in a volume  $V$  is well-defined, no matter how small the volume  $V$ .

We may wonder if the inference to *A* and *B* may be achieved from a weakened form of the ideal gas law whose statement does not presume a density of components. Consider phenomena in which the local form of the ideal gas law (2) is replaced by the relation

$$P = AkT, \tag{2}$$

where  $A$  is some parameter independent of the system’s volume that we would seek to interpret as a density of components in space. If we already know that the system consists of finitely many, spatially localized components, that interpretation of the parameter  $A$  is unproblematic. (We shall see this illustrated in Section 2.3 below in Arrhenius’ analysis of dissociation.)

If we do not already know the system consists of finitely many spatially localized components, however, one example shows that the interpretation is ill-advised. Consider the energy density of classical radiation at frequency  $\nu$ , as given by the Raleigh–Jeans distribution,  $u(\nu, T) = (8\pi\nu^2/c^3)kT$ . To avoid the energy divergence of the ultraviolet catastrophe, let us presume that the interactions between the radiation modes and other thermal systems is so contrived as to preclude excitation of radiation modes with a frequency greater than a cutoff frequency  $\Omega$ . Then the energy density across the spectrum at temperature  $T$  is

$$u(T) = \int_0^\Omega \frac{8\pi\nu^2}{c^3} kT \, d\nu = \frac{8\pi\Omega^3}{3c^3} kT.$$

For classical, isotropic radiation, the radiation pressure is  $P = u/3$ , so that the pressure exerted is<sup>6</sup>

$$P = (1/3)(8\pi\Omega^3/3c^3)kT.$$

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<sup>6</sup>In developing the thermodynamics of classical heat radiation with a frequency cutoff  $\Omega$ , one must treat the frequency cutoff  $\Omega$  as a variable that can alter in processes. It must alter in reversible adiabatic expansions and contractions of radiation in a vessel, in response to the Doppler shifting of the radiation; otherwise, energy will be lost or gained other than through work performed by the radiation pressure on the vessel walls. For a reversible adiabatic expansion, the standard analysis of Wien’s displacement law holds (Planck, 1914, Ch. III): the quantities  $\Omega^3 V$  and  $T^3 V$  remain constant. Thus  $d(T^3 V) = 0$ , so that  $dT = -(T/3V)dV$ , where the differential operator  $d$  represents differential changes in the expansion. Thus the change of energy  $E = u(T)V$  of a volume  $V$  of radiation is  $dE = (8\pi k/3c^3)d(\Omega^3 V T) = (8\pi k/3c^3)(\Omega^3 V)dT = -(1/3)(8\pi\Omega^3/3c^3)(kT)dV = -(1/3)u(T)dV$ . Comparing this last expression with  $dE = -PdV$ , we read off the expression for radiation pressure in the main text.

While the factor  $(1/3)(8\pi\Omega^2/3c^3)$  is related to the density of normal modes of radiation over the frequency spectrum, that factor is not a density of spatially localized components, since the normal modes are extended in space. And that same factor is not a density of components *in space*, but a count of normal modes that will be the same for a system of radiation no matter what its spatial size.

Thus, the use of the ideal gas law as a signature of finitely many, spatially localized components is very restricted. We shall see below in Section 4 that Einstein's new signature in his miraculous argument is significantly more powerful in that it is able to support an inductive inference back to both *A* and *B*.

### 2.3. *Van't Hoff law of osmotic pressure*

In the case of a dilute solution, the simple argument becomes applicable when the solution is sufficiently dilute for interactions between solute molecules to be negligible. Then we apply the argument to the thermal sub-system consisting of just the solute molecules. We recover the result that the pressure it exerts—the osmotic pressure—conforms to the ideal gas law; that is, the pressure is related to the amount of solute, volume and temperature in the same way as ideal gases in (3). That each solute molecule is also in thermal equilibrium with the much larger system of solvent molecules does not affect the argument. We see why we need not be puzzled that the dynamics of solute molecules are quite unlike the free motions of a very dilute, ideal gas.

One of the earliest and most important clues that the ideal gas law was not just a regularity manifested by certain gases came with van't Hoff's recognition in the 1880s of this property of the osmotic pressure of dilute solutions. It is not clear to me, however, exactly when the more general, molecular understanding of the basis of the ideal gas law entered the literature outside Einstein's corpus. *Van't Hoff's analysis (1887)* was given in thermodynamic, not molecular, terms, using the familiar device of a thermodynamic cycle to arrive at the result. This preference for a thermodynamic rather than molecular treatment of van't Hoff's law, as it was soon called, persisted. Nernst, in his *Theoretical Chemistry* (1923, p. 135), still felt compelled to introduce the entire subject of dilute solutions with the remark that "... although most of the results in this field were obtained independently of the molecular hypothesis, yet the study of the properties of dilute solutions has led to a development of our conceptions regarding molecules..." presumably to prevent readers missing the important molecular consequences of the field.<sup>7</sup> Nonetheless, a few pages later (p. 153), Nernst developed a thermodynamic rather than molecular treatment of the foundations of van't Hoff's law. The essential property was that very dilute solutions have a zero heat of dilution—that is no heat is released or absorbed when they are further diluted with solvent. This, Nernst showed, was the necessary and sufficient condition for the law.<sup>8</sup>

<sup>7</sup>Planck (1926, p. 212) introduced an almost identical remark on an intermediate result concerning osmotic pressure: "It is particularly noteworthy that the relation which has been deduced is independent of all molecular assumptions and presentations, although these have played an important role in the development of the theory."

<sup>8</sup>To get a flavor of the reasoning, note that a zero heat of dilution entails that the internal energy  $U$  of system of solute molecules is independent of volume. So, using standard notation, for a reversible, isothermal compression by means of a semipermeable membrane, we have  $0 = (\partial U/\partial V)_T = T(\partial S/\partial V)_T - P$ . A standard thermodynamic relation is  $(\partial S/\partial V)_T = (\partial P/\partial T)_V$ , from which we recover that  $(\partial P/\partial T)_V = P/T$ . This last equation can be solved to yield  $P = \text{const } T$ , with the constant an undermined function of the mass of solute and its volume.



Curiously, Nernst did not remark on the entirely obvious molecular interpretation of this condition. It immediately shows that the solute molecules cannot be interacting through any distance dependent force. For, if they were, energy would be liberated or absorbed when dilution increased the distance between the molecules, according to whether the forces are repulsive or attractive. So it is the smallest step to re-express Nernst's necessary and sufficient condition as an independence of the molecules of the solute. That it is necessary entails that any system manifesting the ideal gas law must conform to it, so that conformity to the ideal gas is the signature of the independence of the solute molecules.

While there is an evident reluctance to understand van't Hoff's law in molecular terms, there was a second eminently molecular use of it. The result was part of a large repertoire of techniques used to infer to the various properties of molecules, such as their molecular weight (See Nernst, 1923, p. 301). Since the osmotic pressure of dilute solutions depended just on the number of molecules in solution, one could infer directly from the osmotic pressure to that number. A celebrated use of this inference was early and immediate. Arrhenius (1887) used it to determine the degree of dissociation of electrolytes in solution. For example, when hydrogen chloride HCl dissolved in water, if it dissociated fully into hydrogen and chloride ions, it would have twice as many dissolved components and thus twice the osmotic pressure as an undissociated hydrogen chloride. Indeed the degree of dissociation could be determined by locating the position of the actual osmotic pressure between these two extremes. (In effect Arrhenius is simply interpreting the parameter  $A$  of an empirically determined expression for osmotic pressure of form (2') as a density of components.) In introducing the technique, Arrhenius (p. 286) remarked that an analogous technique was already standard for determining the degree of dissociation of molecules in gases: an apparent deviation from Avogadro's law could be explained by the dissociation of the gas molecules.

What these few examples show is that well before 1905 there was a healthy tradition of work that inferred the molecular and atomic constitution of substances from their macroscopic, thermodynamic properties. Properties such as the ideal gas law and van't Hoff's law provided a bridge between the microscopic and macroscopic, which could be crossed in both directions. Einstein's miraculous light quantum argument of 1905 belongs to this tradition. It added a new and more powerful bridge to the repertoire and supplied a most audacious application of it. Rather than inferring just to the number of the components, Einstein now inferred to their independence and that they are spatially localized, the latter in direct contradiction with the dominant view that his systems of radiation were composed of waves.

### **3. Einstein on independent components and the ideal gas law**

#### *3.1. Microscopic motions manifest as macroscopic pressures*

Einstein had no reservations about explaining the generality of the application of the ideal gas law in molecular terms. This was a major theme of his dissertation (1905b) and Brownian motion paper (1905c). Part of that explanation was a qualitative idea, that the random thermal motions of components on the microscopic level are manifested macroscopically as a pressure. Or, to put it another way, the same process could be given two interchangeable descriptions, one microscopic and the other macroscopic. The

averaged tendency of components to scatter because of their thermal motions (microscopic description) is also manifested as a pressure, be it the pressure of an ideal gas or the partial pressure of a gas in a mixture or the osmotic pressure of a solute in solution (macroscopic description).

Einstein went to some pains in his dissertation to make the interchangeability of these descriptions acceptable.<sup>9</sup> The vehicle for this effort was consideration of a concentration gradient sustained by some external force, just as in Section 2.1 above. (There I described the force as a gravitational force solely to make it more concrete.)

... the osmotic pressure has been treated as a force acting on the individual molecules, which obviously does not agree with the viewpoint of the kinetic molecular theory; since in our case—according to the latter—the osmotic pressure must be conceived as only an apparent force. However, this difficulty disappears when one considers that the (apparent) osmotic forces that correspond to the concentration gradients in the solution may be kept in (dynamic) equilibrium by means of numerically equal forces acting on the individual molecules in the opposite direction, which can be easily seen by thermodynamic methods.

The osmotic force acting on a unit mass  $-(1/\rho)(\delta p/\delta x)$  can be counterbalanced by the force  $-P_x$  (exerted on the individual dissolved molecules) if

$$-(1/\rho)(\delta p/\delta x) - P_x = 0.$$

Thus, if one imagines that (per unit mass) the dissolved substance is acted upon by two sets of forces  $P_x$  and  $-P_x$  that mutually cancel out each other, then  $-P_x$  counterbalances the osmotic pressure, leaving only the force  $P_x$ , which is numerically equal to the osmotic pressure, as the cause of motion. The difficulty mentioned above has thus been eliminated.<sup>10</sup>

Einstein also invoked the interchangeability of descriptions in his Brownian motion paper. The essential presumption of that paper was that the molecular kinetic approach must apply equally well to solutes in solution, as to microscopically visible particles in suspension. Therefore, they must exhibit random thermal motions, just like solute molecules. But, because of the size of the particles, these motions would now be visible under the microscope, the cardinal prediction of the paper. In the first section of the paper, Einstein turned to a redescription of these random thermal motions. Just as with solutes, he asserted, the averaged scattering tendencies produced by these motions must also be manifested as a pressure that conforms to the same laws as govern the osmotic pressure of solutes. There are two parts to this assertion. First is the idea that a random thermal motion can be manifested as some sort of a pressure. This is not so startling an idea, even for particles visible under the microscope. Second is the idea that the pressure of these

<sup>9</sup>It strikes me as odd that Einstein would put special effort into justifying this assumption while neglecting the many other questionable assumptions in his dissertations (e.g. sugar molecules are not perfect spheres and the dissolving medium of water is not a perfectly uniform fluid at these scales). Uffink (2006) may have made the decisive point when he noted that an overall neglect of statistical physics in Einstein's dissertation may have been an accommodation to Einstein's dissertation director, Alfred Kleiner, who, Uffink conjectures, may have harbored objections to the kinetic approach.

<sup>10</sup>Einstein's footnote: "A detailed presentation of this line of reasoning can be found in *Ann. d. Phys.* 17, p. 549, 1905."

particles quantitatively obeyed the same laws as those obeyed by solutes. Recognizing that his readers may not be so comfortable with this latter idea, Einstein hedged a little:

...it is difficult to see why suspended bodies should not produce the same osmotic pressure as an equal number of dissolved molecules...

He then took the bull by the horns and immediately sketched the result:

...We have to assume that the suspended bodies perform an irregular, albeit very slow, motion in the liquid due to the liquid's molecular motion; if prevented by the wall from leaving the volume  $V^*$  [of suspending liquid], they will exert a pressure upon the wall just like the molecules in solution. Thus, if  $n$  suspended bodies are present in the volume  $V^*$ , i.e.  $n/V^* = v$  in a unit volume, and if neighboring bodies are sufficiently far separated from each other, there will be a corresponding osmotic pressure  $p$  of magnitude

$$p = RT/V^*n/N = RT/Nv,$$

where  $N$  denotes the number of actual molecules per gram-molecule...

Einstein recognized that mere assertion may not be enough to convince readers that the laws governing this pressure would remain completely unaltered as we scale up the size of particles by perhaps three orders of magnitude. So he promised them something a little stronger:

...It will be shown in the next section that the molecular-kinetic theory of heat does indeed lead to this broader interpretation of osmotic pressure.

Before we turn to this derivation in Section 3.2 below, we should note that the interchangeability of the two descriptions was central to Einstein's arguments in both his dissertation and the Brownian motion paper. The most important application came in Einstein's derivation of his expression for the diffusion coefficient  $D$  for diffusing sugar molecules or suspended particles undergoing Brownian motion, where both are modeled as spheres of radius  $r$  in a continuous medium of viscosity  $\mu$ . The derivation appears in slightly different forms in the dissertation (1905b, Section 4) and the Brownian motion paper (1905c, Section 3).

In the more straightforward form of the dissertation, Einstein considered a concentration gradient  $\partial\rho/\partial x$  along which the molecules diffuse because of their thermal motions. He immediately moved to the macroscopic re-description: the forces driving the molecules are the forces of the osmotic pressure gradient  $\partial p/\partial x$ . So the force  $K$  on an individual molecule is  $K = -(m/\rho N)(\partial p/\partial x)$ , where  $\rho$  is the mass density,  $m$  the mass of the molecule and  $N$  Avogadro's number. Einstein now assumed that the solution was dilute so that the osmotic pressure obeyed the ideal gas law  $p = (R/m)\rho T$ , with  $R$  the ideal gas constant. Finally, the osmotic pressure forces were assumed perfectly balanced by the viscous forces acting on a perfect sphere moving through a fluid of viscosity  $\mu$  with speed  $\omega$ , as given by Stokes' law  $K = 6\pi\mu\omega r$ . Combining these equations, Einstein recovered an expression that related the mass flux due to diffusion  $\rho\omega$  to the concentration gradient,  $\partial\rho/\partial x$ , which was  $\rho\omega = -(RT/6\pi\mu)(1/Nr)(\partial\rho/\partial x)$ . Since the diffusion coefficient  $D$  is defined by  $\rho\omega = D(\partial\rho/\partial x)$ , Einstein could read off his result:

$$D = (RT/6\pi\mu)(1/Nr). \quad (4)$$

This relation (4) is central to both papers. In his dissertation, it was one of the two relations in the two unknowns  $N$  and  $r$  that Einstein solved to find the size of  $N$ , the ultimate goal of his paper. In the Brownian motion paper, the diffusion coefficient fixed the variance of the random motions of the suspended particles. So the relation (4) allowed Einstein to predict the size of these motions from known values of  $N$ ; or, conversely, it allowed him to proceed from the observation of the size of the motions to an estimate of  $N$ .

### 3.2. *A quantitative expression for the relation*

We see in the above derivation of his expression for the diffusion coefficient that a qualitative relationship between microscopic thermal motions and a macroscopic pressure was not enough. Einstein needed a particular quantitative expression for it in the cases at issue, and that was the ideal gas law.

The simple argument of Section 2.1 above already sketches how this law can be recovered using the approach Einstein outlined in his dissertation, where he proposed we consider osmotic pressure equilibrated by an external force field. The microscopic tendency of components to scatter because of their thermal motions is governed by the Boltzmann factor  $\exp(-E/kT)$ . If the distribution of components does not match that factor, then random motions of the components will have the effect of driving the distribution towards this equilibrium distribution. This tendency is redescribed macroscopically as a pressure. Following Einstein's approach, that pressure is checked by an external force field. We can then read the magnitude of the pressure from the condition of equilibrium of forces. The outcome is that, in the context of the molecular kinetic theory, the microscopic fact of component independence is expressed in the macroscopic fact of the ideal gas law.

Einstein's alternative derivation of this same result is given in Section 2 of the Brownian motion paper. It is more elaborate and more precise, but in concept essentially the same. It begins with the statistical mechanics of many independent components and ends with the pressure associated with their thermal motions. The microscopic fact of independence is once again expressed macroscopically as the ideal gas law. In slightly modernized notation, it proceeds as follows. Einstein first recalled the essential results of his 1902–1903 development of statistical mechanics. He posited a state space with what we would now call canonical variables  $p_1, \dots, p_l$ . The entropy  $S$  of a system whose states are Boltzmann distributed (according to (9) below) is given by

$$S = \bar{E}/T + k \ln \int \exp(-E/kT) dp_1 \dots dp_l, \quad (5)$$

where  $E(p_1, \dots, p_l)$  is the energy of the system at the indicated point in the state space. Its free energy  $F$  is given by

$$F = \bar{E} - TS = -kT \ln \int \exp(-E/kT) dp_1 \dots dp_l. \quad (6)$$

Einstein now applied these relations to a system consisting of  $n$  components in a volume  $V$  of liquid, enclosed by a semi-permeable membrane. The components could be either solute molecules or suspended particles. Einstein sought to establish how expression (6) for free energy is specialized by the assumption that the components are (i) independent of one another, (ii) free of external forces and (iii) that the suspending liquid is homogeneous. To this end, he chose a particular set of state space coordinates. The Cartesian spatial

coordinates of the centers of mass of components  $1, \dots, n$  are  $x_1, y_1, z_1; x_2, y_2, z_2; \dots; x_n, y_n, z_n$ . For notational convenience, I will write the collected set of these  $3n$  coordinates as “ $x$ ”. Although Einstein did not mention them explicitly, I will represent a corresponding set of  $3n$  conjugate momentum coordinates as “ $\pi$ .”

Modern readers would have little trouble recognizing that Einstein’s specializing assumptions entail that the energy  $E(x, \pi)$  in (6) is independent of the spatial coordinates  $x$ . As a result, the free energy can be re-expressed as

$$F = -kT \ln \left[ \int \exp(-E(\pi)/kT) d\pi \int dx \right], \tag{7}$$

where the integrations extend over accessible values of the coordinates. Since  $V = \int dx_1 dy_1 dz_1$  and so  $V^n = \int dx_1 dy_1 dz_1 \dots dx_n dy_n dz_n = \int dx$  this last expression can be rewritten as

$$F = -kT[\ln J + n \ln V], \tag{8}$$

where  $J = \int \exp(-E(\pi)/kT) d\pi$  in independent of  $x$ .

Einstein apparently did not expect his readers to find it so straightforward that the transition from (6) to (8) expresses the intended independence. (Perhaps, after decades of quantum theory, modern readers are more comfortable reading independence in terms of the vanishing of interaction energies.) So Einstein expressed the independence in probabilistic terms and spent about a full journal page developing the result. In brief, he noted that the Boltzmann factor  $\exp(-E/kT)$  in (6) figures in the expression for the probability distribution of the components. The probability density is

$$p(x, \pi) = \exp(-E(x, \pi)/kT)B, \tag{9}$$

where  $B = \int \exp(-E/kT) dx d\pi$  normalizes the probabilities to unity. The probability that the  $n$  components are located in the small volume  $dx = dx_1 dy_1 dz_1 \dots dx_n dy_n dz_n$  of ordinary space is

$$dP = dx \int \exp(-E(x, \pi)/kT) d\pi = dxJ(x).$$

The requirement of independence of the components in space—that each such small volume be equally probable—immediately entails that  $J(x) = \int \exp(-E(x, \pi)/kT) d\pi = J$  is independent of  $x$ . It now follows that the integrations over the conjugate momentum coordinates  $\pi$  and the Cartesian spatial coordinates  $x$  in (7) can be separated and expression (8) for  $F$  recovered.

With expression (8) established, the recovery of the pressure  $p$  exerted by the thermal motions of the components required only the use of the thermodynamic relation

$$P = - \left( \frac{\partial F}{\partial V} \right)_T. \tag{10}$$

Substituting for  $F$  using (8), we recover

$$P = kT \frac{\partial}{\partial V} \Big|_T [\ln J + n \ln V] = \frac{nkT}{V}.$$

That is  $PV = nkT$ , the ideal gas law.

The simple argument of Section 2.1 and this argument differ essentially only in the probe used to find the pressure associated with random thermal motions. In the simple argument, the probe is a force field that permeates the thermal system, as suggested by Einstein in his dissertation. The argument of Einstein's Brownian motion paper in effect uses the restraining forces of a containing vessel to probe the pressure forces, for the expression for pressure (10) is routinely derived by considering the change of free energy with volume of a thermal system enclosed in a vessel in a reversible expansion (as described in Section 5.1 below).

### 3.3. *The background in Einstein's "worthless" first papers on intermolecular forces*

Einstein was well prepared for the analyses just sketched. In 1901 and 1902, he had published two papers in which he advanced what he called "the simplest possible assumptions about the nature of the molecular forces of attraction" (1901, pp. 514–515). Drawing on an analogy with gravitational forces, the forces between two molecules separated by a distance  $r$  were assumed to be governed by a potential  $P$  satisfying

$$P = P_{\infty} - c_1 c_2 \varphi(r), \quad (11)$$

where  $c_1$  and  $c_2$  are constants characteristic of the two types of molecules and  $\varphi(r)$  is a universal function, the same for all types of molecules. Einstein's two earliest papers (1901, 1902a) were devoted to developing this hypothesis and to seeking ways of testing it and estimating its characteristic constants  $c_i$ . In Einstein scholarship, these papers are generally passed over in haste (Pais, 1982, pp. 56–57), if they are noticed at all,<sup>11</sup> reflecting Einstein's own dismissal of the papers as "worthless."<sup>12</sup>

While the content of these papers has had no direct effect on later science, they prepared Einstein well for the work of 1905 in two aspects. In the second paper, Einstein introduced the device of equilibrating osmotic pressure and ordinary gas partial pressure by external forces. His reason for introducing the device was explained carefully in the introductory page of Einstein (1902a). The traditional theoretical device for exploring the properties of solutions and gas mixtures was the semi-permeable membrane—a membrane presumed perfectly permeable to one type of molecule, but not another. Einstein doubted that such membranes were physically realizable. He proposed that we replace them by conservative forces that are able to act differentially upon the different types of molecules present. Einstein clearly felt that the idea was a significant extension of existing theory, for he concluded the first section of the 1902 paper by stating it rather formally as a proposition. First he formulated the proposition that thermodynamic analysis may employ semi-permeable membranes:

...on the basis of our prior experience, we may in any case assert the proposition: one remains in conformity with experience if one extends the second law of thermodynamics to physical mixtures whose individual components are confined to certain parts of space by conservative forces acting in certain surfaces.

<sup>11</sup>But see "Einstein on the Nature of Molecular Forces" pp. 3–8 in Papers, Vol. 2.

<sup>12</sup>"...I am sending you all my publications excepting my two worthless beginner's works..." (to Stark, 7 December 1907, Papers, Vol. 5, Doc. 66).

This he extended to the case of forces distributed throughout the volume of the system

We generalize this proposition hypothetically to the following: One remains in agreement with experience if one applies the second law of thermodynamics to physical mixtures upon whose individual components arbitrary conservative forces act.

Einstein proceeded to use these conservative forces in the course of the paper to develop his principal results. It was essential to his analysis that different types of molecules could be acted upon by different forces. For the forces must be able to maintain in thermal equilibrium a solution in which metallic salts of different acids are segregated to two parts of the solution, with an intermediate mixed zone in between. (This was the system investigated in Section 3 of his paper.) Gravitational forces, such as were employed in the simple argument above, will not suffice for his purposes, as Einstein explicitly noted (Einstein, 1902a, p. 802) in the context of a different example.

When Einstein later suggested in his dissertation that we could analyze osmotic pressure by means of a counterbalancing force field, he was reviving more casually an idea that he had already exploited extensively in far more complicated circumstances. In his 1902 paper, he routinely considered solutions with many types of ions, each with their own equilibrating force field, in solvents of different types, and, at the same time, with the electrical potentials of electrolysis acting upon the charged ions. One process he considered in this very complicated context was diffusion. Even though the relation to this earlier work is quite evident to anyone who reads both papers, Einstein gave no citation to his paper of 1902 in his dissertation or in his Brownian motion paper indicating the relation. Here we have yet another illustration of Einstein's well known inclination not to cite his sources, but this time the connection that was lost is to his own work.

The second way in which these papers of 1901 and 1902 prepared Einstein for his papers of 1905 lay in the overall project of these earlier papers. Einstein was concerned to establish empirically the model for intermolecular forces of Eq. (11). Both papers of 1901 and 1902 are essentially concerned with how the existence and character of intermolecular forces are expressed in experimentally measurable quantities. He chose two domains of experiment to seek these quantities: in capillary action (1901) and in electrolysis (1902). A special concern lay in the determination of the theoretical coefficients  $c_i$  from them. The analysis of 1902 proved complicated, with Einstein concluding that the electrical potential difference between a metal and the completely dissociated solution of a salt depended in a particular way upon the nature of the solvent, this being a result that could give empirical access to the forces of (11). Einstein felt the imbalance between theory and experiment so great that he concluded the paper by "...apologiz[ing] for sketching such a skimpy plan for laborious investigation without myself contributing something to the experimental solution..."

That Einstein was driven to such complicated constructions shows how much he must have reflected upon the problem of how the existence and character of intermolecular forces are expressed empirically. These early reflections must in turn have prepared Einstein well to deal with the simplest case, the absence of forces between the components of a thermal system. Yet that is just the case that arises throughout his statistical papers of 1905, with the regard to solute molecules in his dissertation, suspended particles in the Brownian motion paper and finally light quanta.

#### 4. Einstein's light quantum paper

The centerpiece of Einstein's light quantum paper (1905a) is a demonstration that the thermodynamic properties of high-frequency heat radiation bear the characteristic signature of finitely many, spatially localized, independent components that he calls energy quanta or light quanta. The argument that establishes this has two parts. The first is a specialization of Boltzmann's principle to the case of fluctuations of the spatial volume of a thermal system. The second is its application to high-frequency heat radiation.

##### 4.1. Boltzmann's principle

What Einstein called Boltzmann's principle is encapsulated in the equation chiseled into Boltzmann's gravestone: " $S = k \log W$ ". The difficulty with the application of the principle is that its terms, the entropy  $S$  and the probability  $W$ , are rarely defined precisely. Of what is  $W$  the probability? We cannot say, without some account of the conditions surrounding the generation of the outcome.<sup>13</sup> Is  $S$  the entropy of an equilibrium state as defined by Clausius' original definition for entropy change

$$S - S_0 = \int dq_{\text{rev}}/T, \quad (12)$$

where  $q_{\text{rev}}$  is the heat transferred to an equilibrium thermodynamic system during a reversible process? In this case, assuming that the probability  $W$  has a meaning independent of the formula  $S = k \log W$ , Boltzmann's principle is a factual result that requires proof. Or is  $S$  the entropy of a non-equilibrium state? In this case, Clausius' definition is no longer applicable and Boltzmann's principle may be nothing more than a definition that extends the use of the term "entropy" to non-equilibrium systems.<sup>14</sup>

In Section 5 of his light quantum paper, Einstein used a relative form of Boltzmann's principle and the way he used it largely makes clear how he would answer the above questions concerning  $S$  and  $W$  in this case. For two states with entropies  $S$  and  $S_0$  and relative probability  $W$ , the principle asserts

$$S - S_0 = k \ln W, \quad (13)$$

It becomes apparent from the subsequent application that Einstein intended the two states to be ones that can be transformed into each another by the normal time evolution of the systems, so that in general the two states are not equilibrium states, but could include non-equilibrium states momentarily arrived at by a fluctuation from an equilibrium state. The probability  $W$  is just the probability of the transition between the two states under the system's normal time evolution. It also becomes clear that, even if the states are non-equilibrium states arrived at through a rare fluctuation, Einstein intended that the states also be describable by the same means as are used to describe equilibrium states.

Finally, Einstein assumed that the entropy of one of these non-equilibrium states, computed by means of Boltzmann's principle (13), would agree with the entropy of the corresponding equilibrium state, computed through the Clausius equilibrium formula (12).

<sup>13</sup>Analogously we cannot say that coin has a probability of 1/2 of showing a head if all we know is that there is a coin. We can say it, however, if we know the coin is fair and that it was tossed.

<sup>14</sup>Readers who think that these sorts of ambiguities are minor nuisances unlikely to produce major problems should see Norton (2005).



That Einstein intends all this becomes clear from the subsequent application of the formula (13) in Section 5 of his paper. Einstein considered a system consisting of a volume  $V_0$  of space containing  $n$  non-interacting, moving points, whose dynamics are such as to favor no portion of the space over any other. The second state is this same system of points, but now confined to a sub-volume  $V$  of  $V_0$ . It followed immediately that the probability of transition under normal time evolution from the state in which all of volume  $V_0$  is occupied to one in which just  $V$  is occupied is

$$W = (V/V_0)^n. \quad (14)$$

Therefore, from (13), the corresponding entropy change for this fluctuation process is just

$$S - S_0 = kn \ln(V/V_0). \quad (15)$$

From the above development, it is clear that the state with entropy  $S$  is a non-equilibrium state, arrived at through a highly improbable fluctuation. There is a corresponding equilibrium state: the system consisting of the  $n$  components at equilibrium and now confined to the sub-volume  $V$  by a partition. It becomes clear that Einstein intended the entropy  $S$  recovered from (15) to agree with the entropy of this corresponding equilibrium state as given by the Clausius formula (12). For when Einstein applied this formula (15) to the cases of an ideal gas and also high-frequency heat radiation (in Section 6), the states of which  $S$  and  $S_0$  are the entropies are the equilibrium states occupying the volumes  $V$  and  $V_0$ , with their entropies determined through the Clausius formula (12).

What is most in need of justification is this presumed agreement between the Clausius entropy (12) of an equilibrium state and the entropy recovered from Boltzmann's principle (13) for a non-equilibrium state with the same macroscopic description. In this section, Einstein gave a much-celebrated derivation of Boltzmann's principle that proceeds from the idea that the entropy of a state must be a function of its probability and that, for independent systems, the entropies must add while the probabilities multiply. The log function is the unique function satisfying this demand. What this demonstration shows is that, *if there is any admissible relationship between entropy  $S$  and probability  $W$* , then it must be  $S = k \log W$  in order that entropies add when probabilities multiply. This derivation does not supply a demonstration of the agreement of the two senses of entropy, for there may be no admissible relationship between  $S$  and  $W$  at all.<sup>15</sup>

#### 4.2. *The miraculous argument*

Einstein's relation (15) is a new, macroscopic signature of the microscopic constitution of many independent, spatially localized components: the entropy of a state varies logarithmically with its spatial volume. In his miraculous argument, Einstein establishes

<sup>15</sup>Presumably this problem could be resolved by drawing on Einstein's earlier papers in the foundations of statistical physics of 1902–1904 (Einstein, 1902b, 1903, 1904) and also the new work he promised that was to “eliminate a logical difficulty that still obstructs the application of Boltzmann's principle.” The former papers included his (1903, Section 6) demonstration of the canonical entropy formula (5), which relates Clausius' thermodynamic entropy to statistical quantities. The new work was to replace the use of equiprobable cases of Boltzmann and Planck by the statistical probabilities Einstein favored. If we set the concerns of this new work aside, the problem would seem to be easily resolvable. We associate states, equilibrium or non-equilibrium, with numbers of Boltzmann complexions or, in the more modern vernacular, with volumes of phase space; and the entropy of the states is given by the logarithm of those numbers or volumes. Then the agreement of the two senses of entropy will follow from demonstrations such as Einstein's (1903, Section 6) just mentioned.

that high-frequency heat radiation carries that signature. In Section 4, Einstein laid out the empirical results needed to see the signature. He recalled the formula given by Wien for the energy density  $u(\nu, T)$  of heat radiation of temperature  $T$  at frequency  $\nu$ , which had proven to hold empirically for high-frequency radiation<sup>16</sup>

$$u(\nu, T) = (8\pi h\nu^3/c^3) \exp(-h\nu/kT). \quad (16)$$

Recalling that the entropy density  $\varphi(\nu, T)$  is related to this energy density by the condition  $\partial\varphi/\partial u = 1/T$ , it follows that the entropy density is

$$\varphi = -\frac{ku}{h\nu} \left[ \ln \frac{c^3 u}{8\pi h\nu^3} - 1 \right].$$

Taking the system to be just the portion of radiation in the volume of space  $V$  with frequencies in the interval  $\nu$  to  $\nu + d\nu$ , it follows that the system has entropy

$$S = \varphi V d\nu = -\frac{kE}{h\nu} \left[ \ln \frac{c^3 E}{8\pi h V \nu^3 d\nu} - 1 \right], \quad (17)$$

where its energy  $E = uV d\nu$ . If we compare two such systems with the same energy  $E$  but occupying volumes  $V$  and  $V_0$  of space, it now follows from (17) that the entropy difference is just

$$S - S_0 = k(E/h\nu) \ln(V/V_0). \quad (18)$$

Therefore, Einstein continued in Section 6, a definite frequency cut of high-frequency heat radiation carries the characteristic macroscopic signature of a system of many spatially independent components, the logarithmic dependence of its entropy on volume, as displayed in (15). Moreover, a comparison of (15) and (18) enabled Einstein to read off the size of the energy quanta. There are  $n = E/h\nu$  quanta. That is, the energy  $E$  of the heat radiation was divided into  $n$  independent, spatially localized quanta of size  $h\nu$ . To be precise, the more cautious wording of Section 6 prefaces this conclusion with the qualification that a relevant system of heat radiation “behaves thermodynamically as if...” or it “behaves, as concerns the dependence of its entropy on volume...”.<sup>17</sup> Presumably, these qualifications were temporary and could be discarded with the further empirical support of photoluminescence, the photoelectric effect and the ionization of gases of Sections 7–9 of the paper. For the introduction to the paper simply asserts that a propagating light ray “consists of a finite number of energy quanta localized at points of space that move without dividing, and can be absorbed or generated only as complete units.”

This is truly a miraculous argument. For Einstein had reduced a delicate piece of statistical physics to something quite easy to visualize. The probability that the system of heat radiation fluctuates to the smaller volume is just  $W = (V/V_0)^n = (V/V_0)^{E/h\nu}$ , just as if the system consisted of  $n = E/h\nu$  independently moving points, each of which would have a probability  $V/V_0$  of being in the reduced volume  $V$ . Yet at the same time, the argument delivers the impossible result that the wave theory of light was not completely

<sup>16</sup>As before, I have modernized Einstein’s notation, writing  $k$  for Einstein’s  $R/N$ ,  $h/k$  for Einstein’s  $\beta$  and  $8\pi h/c^3$  for Einstein’s  $\alpha$ .  $h$  is Planck’s constant.

<sup>17</sup>These qualifications may also reflect the fact that Einstein’s inference is inductive and that he supposes that is possible but unlikely that a system not constituted of independent quanta could give the same entropy-volume dependence.

correct after all and that something along the lines of a corpuscular theory would need to be revived.

We can also see immediately that Einstein has found a signature of discreteness more powerful than the ideal gas law. We saw in Section 2.2 above that the ideal gas law is a secure signature of the independence of components, but it is hard to use without circularity to establish that the system is composed of finitely many components (*A.*) and that they are spatially localized (*B.*). Einstein's signature has no difficulty indicating *A.* and *B.* Indeed the indication is so strong as to overturn the presumption of the infinitely many, spatially distributed components of the wave treatment of heat radiation.

In a striking paper, Dorling (1971) has shown that essentially no inductive inference at all is needed to proceed from Einstein's signature to there being finitely many, spatially localized components, although there is no indication that Einstein realized this. Dorling showed that, if we assume that the probability of fluctuation to volume  $V$  is given by  $W = (V/V_0)^{E/h\nu}$ , then we can deduce two results. If  $E/h\nu$  has any value other than  $1, 2, 3, \dots$ , then a contradiction with the probability calculus ensues. For the cases of whole number  $n = E/h\nu$ , with probability one, the energy must be divided into  $n$  spatially localized points, each of the same  $h\nu$ . The probability is not a subjective probability, but the physical probability of the formula  $W = (V/V_0)^{E/h\nu}$ . In other words, this formula tells us that in measure one of infinitely many cases in which we might check the state of the radiation energy  $E$ , it will be distributed in  $n$  spatially localized points of energy of size  $h\nu$ . While he does not assert it, I believe Dorling's approach also establishes the independence of the spatial distribution of the points.

To get a flavor of Dorling's reasoning, take the case of  $n = E/h\nu = 1$ . There is a probability  $1/M$  that all the energy is located completely in some subvolume  $V_0/M$  of  $V_0$ . So if we divide the volume  $V_0$  exhaustively into  $M$  mutually exclusive subvolumes of size  $V_0/M$ , it follows that there is a probability  $M \times (1/M) = 1$  that all the energy is fully contained in one of them. That is, there is probability 1 that all the energy is localized in an  $M$ th part of the volume  $V_0$ . Since  $M$  can be as large as we like, with probability one, the energy must be localized at a spatial point.

## 5. The similarity of light quanta and molecules

### 5.1. Deduction of the ideal gas law for ideal gases

At several points in the discussion, Einstein remarked on the analogy to ideal gases and solutes in dilute solutions. A system of  $n$  such components would fluctuate to a smaller volume according to (14) so that the entropy changes with volume according to (15), a result also known to be correct empirically for the volume dependence of entropy of an ideal gas in its equilibrium state. In a short footnote at the end of Section 5, Einstein showed that the logarithmic dependence of entropy on volume for the equilibrium states enables deduction of the ideal gas law. The argument he gave is a drastically curtailed application of the essential content of the thermodynamic relation (10), which, as we saw above, was also used by Einstein in his Brownian motion paper to recover the pressure of an ideal gas. It is routine to recover that relation for the free energy  $F = E - TS$  by considering a reversible change in which

$$dE = d(\text{heat}) - d(\text{work}) = T dS - P dV,$$

where  $P$  is the pressure over the boundary of the system. For such a change

$$dF = dE - d(TS) = -S dT - P dV = -\left.\frac{\partial F}{\partial T}\right|_V dT - \left.\frac{\partial F}{\partial V}\right|_T dV. \quad (19)$$

Relation (10) is recovered by matching coefficients in  $dV$  in the second equality. Use of the relation can be circumvented by inserting appropriate expressions for  $E$  and  $S$  directly into the expression for  $dF$ . For a reversible isothermal expansion of an ideal gas of  $n$  molecules, we have

$$dF = dE - T dS = -T d(kn \ln V) = -(nkT/V) dV. \quad (20)$$

Comparison of the coefficients of  $dV$  in (20) and (19) yields the ideal gas law  $P = nkT/V$ . Note that the inference of (20) requires one of the characteristic properties of an ideal gas: its internal energy  $E$  is independent of volume and fixed solely by temperature  $T$ , so that  $dE = 0$  for an isothermal process.

Presumably these last inferences are what Einstein intended in his closing remarks of Section 5 that “the Boyle–Gay–Lussac law [ideal gas law] and the analogous law of osmotic pressure can easily be derived thermodynamically<sup>footnote</sup> [from relations (15)].” The footnote appended read:<sup>18</sup>

If  $E$  is the energy of the system, we get,

$$-d(E - TS) = P dV = T dS = nkT/V dV; \text{ thus } PV = nkT.$$

Einstein’s inference requires the property of ideal gases that  $dE = 0$  for  $d$  representing a reversible, isothermal process, else  $P dV$  fails to equal  $T dS$ .

## 5.2. Deduction of the ideal gas law for energy quanta

At this point, one might well wonder why Einstein needed a new signature of independent components. The ideal gas law was just such a signature already explored thoroughly in Einstein’s other statistical work of 1905. Indeed Einstein repeatedly stressed the closeness of the cases of his energy quanta and ideal gases. And now Einstein has shown that the logarithmic dependence of entropy on volume delivers the ideal gas law. So why did Einstein resort to a new signature?

There is an easy answer that does not bear scrutiny. One might think that heat radiation just does not satisfy the ideal gas law. For, according to the ideal gas law, the pressure of a gas drops if the volume is increased isothermally. Yet for heat radiation, this does not happen. The pressure it exerts depends only on intensive quantities like its temperature and not on its volume. For full spectrum heat radiation, the pressure is simply one third the energy density,  $P = u/3$ , where the energy density is fixed by the temperature. So its pressure remains constant in an isothermal expansion.

Yet—despite these appearances—high-frequency heat radiation *does* obey the ideal gas law. To see this, first take the case of full spectrum heat radiation, where the heat radiation is presumed to satisfy the Wien distribution law (16). Integrating (16) over all frequencies, we find that the total energy density is  $u = \sigma T^4$ , for  $\sigma$  a constant. By familiar arguments,<sup>19</sup> we recover the radiation pressure  $P = u/3$ . Einstein showed in Section 6 of his light

<sup>18</sup>With modernized notion and correction of a typographical error.

<sup>19</sup>Since  $dS/dE = 1/T$ , the entropy  $S$  of a volume  $V$  of radiation with energy  $\sigma T^4 V$  is  $(4/3)\sigma T^3 V$ . Hence its free energy  $F = E - TS$  is  $-\sigma T^4 V/3$ , so that the radiation pressure is  $P = -(\partial F/\partial V)_T = \sigma T^4/3 = u/3$ .

quantum paper (see Section 5.5 below) that the average energy of a quantum for this full spectrum case is  $3kT$ . Therefore the total number  $n$  of quanta in a volume  $V$  of radiation is  $n = uV/3kT$  or  $u = 3nkT/V$ . Hence

$$P = u/3 = 3nkT/3V = nkT/V,$$

which is just the ideal gas law.

An analogous analysis yields the same result for a single frequency cut of high-frequency heat radiation. Consider a volume  $V$  containing such a frequency cut with energy  $E = uV dv$ . It follows by direct computation<sup>20</sup> from (16) and (17) that the free energy  $F$  of the system is given by  $F = uV dv (-kT/hv)$ . Once again

$$P = -\left.\frac{\partial F}{\partial V}\right|_T = -\left.\frac{\partial}{\partial V}\right|_T \left( uV dv \frac{-kT}{hv} \right) = \frac{u dv}{hv} kT = \frac{nkT}{V}. \tag{21}$$

since the number of quanta per unit volume  $n/V = u dv/hv$ .

### 5.3. Disanalogies

The reason that we readily overlook that high-frequency heat radiation satisfies the ideal gas law is there is an important disanalogy with ideal gases. In an ideal gas, the number of component molecules is fixed. So, in an isothermal expansion, the density of these component molecules drops as the fixed number of components is spread over a greater volume. For heat radiation, however, the number of components is not fixed. In each frequency cut with energy  $E$ , the number of quanta is  $E/hv$ , where the energy  $E = u(v, T)V$ . So, in an isothermal expansion, the number of quanta increases in direct proportion to the volume  $V$  and the density of quanta remains fixed. The ideal gas law only predicts a drop in pressure in an isothermal expansion under the assumption that the number of components is fixed and not growing in direct proportion to the volume  $V$ .

Similarly, a heating of a full spectrum system of heat radiation creates quanta, in proportion<sup>21</sup> to  $T^3$ . So, under a constant volume heating, the radiation pressure will increase in proportion to  $n(T)T$ , that is, in proportion to  $T^3 T = T^4$ , as we expect since  $p = u/3 = \sigma T^4/3$ .

This variability of the number of component quanta is associated with another disanalogy between ideal gases and quanta. Recall that the deduction in (20) of the ideal gas law from the logarithmic dependency of entropy upon volume required a further assumption. It was that the energy  $E$  of an ideal gas is unchanged in an isothermal expansion. This assumption fails for a system of energy quanta; the number of quanta and thus the energy  $E$  will increase in direct proportion to the volume  $V$  during an isothermal heating.

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<sup>20</sup> $F = E - TS = uV dv - T \left( -\frac{kuV dv}{hv} \left[ \ln \frac{c^3 u}{8\pi h v^3} - 1 \right] \right) = uV dv + \frac{uV dv kT}{hv} \left( \frac{-hv}{kT} - 1 \right) = -uV dv \frac{kT}{hv}$ .

<sup>21</sup>To see this, note that the number of quanta  $n$  in a volume  $V$  is

$$\frac{n}{V} = \int \frac{u(v, T)}{hv} dv = \int \frac{8\pi v^2}{c^3} \exp\left(-\frac{hv}{kT}\right) dv = \left(\frac{kT}{h}\right)^3 \int \frac{8\pi}{c^3} \left(\frac{hv}{kT}\right)^2 \exp\left(-\frac{hv}{kT}\right) d\left(\frac{hv}{kT}\right)$$

$T^3$  dependence for  $n$  follows, since the final integral will be some definite number independent of  $T$ .

So how is it possible for us to recover the ideal gas law for systems of quanta? The deduction in (20) of the ideal gas law for ideal gases also depended upon the assumption that, for an isothermal expansion  $d$ , the entropy  $S$  varies as  $dS = d(nk \ln V) = nk/V dV$ . That fails for a system of quanta for an isothermal expansion. For we see from (17) that the entropy of a single frequency cut of high-frequency radiation does depend logarithmically on its volume. However we see from (17) that the entropy also depends in a more complicated way on the energy  $E$  and that energy  $E$  in turn contains a volume dependency. So the volume dependency of entropy is more complicated for heat radiation than for an ideal gas. This greater complexity was masked in the case of Einstein's miraculous argument, since the two states connected by the fluctuation process of (14) and (15) have the same energy. The process is simply the chance accumulation of many, non-interacting points. Therefore only the direct dependence of entropy on volume  $V$  of (17) was evident and not the indirect dependence on  $V$  through  $E$ . As a result, that  $E$  does depend on the volume  $V$  in an isothermal process alters the calculation of pressure in (20) in two places—the expressions for both  $dE$  and  $dS$ —and the alterations cancel to enable the recovery of the ideal gas law.

This last effect reveals the final disanalogy between ideal gases and the quanta of heat radiation. In the case of ideal gases, the two equilibrium states related by equation (15) can be connected by an isothermal compression: the entropy change  $S-S_0$  results when an ideal gas of  $n$  molecules is compressed isothermally and reversibly from a volume  $V_0$  to a volume  $V$ . The same is not true of a system of quanta. Consider the conditions placed on a single frequency cut of heat radiation for the two states of Eq. (15). The energy  $E$  of both states must be the same, even though the volumes occupied differ. Therefore, the energy densities of the two states are different. Now the energy density  $u(\nu, T)$  of heat radiation is a function of the frequency  $\nu$  and temperature  $T$  alone. Since we also suppose that the frequency  $\nu$  of the radiation is the same for both states, it follows that the temperatures associated with the two states must differ.

In short, the end state of a fluctuation in volume by an ideal gas can also be arrived at by a reversible, isothermal compression of the gas. The end state of a fluctuation in volume by a system of quanta cannot be arrived at by an isothermal compression; it requires a process that also changes temperatures.

#### 5.4. *Why the miraculous argument?*

Why did Einstein offer the miraculous argument when, it would seem the more traditional analysis of the ideal gas law seems capable of delivering at least the result of independence of microscopic components? Surely the straightforward answer is correct: Einstein needed to establish more than the independence of the components. He needed to establish that there are finitely many of them and that they are spatially localized. As we saw in Section 2.2, the ideal gas law has great trouble delivering these properties. Einstein's miraculous argument employs a new signature that yields both properties through vivid and simple arguments.

We can see quite quickly how the variability of the number of quanta would make it hard for Einstein to use the ideal gas law to establish the presence of even finitely many components, the energy quanta of size  $h\nu$ . We have from purely thermodynamic considerations in (21) that the pressure exerted by a single frequency cut of radiation is  $P = (u d\nu/h\nu)kT$ . We now recognize that this is a form of the ideal gas law for quanta of

energy  $h\nu$ , since the term  $(u\,d\nu/h\nu)$  is equal to the number of quanta per unit volume,  $n/V$ . But announcing that interpretation of  $(u\,d\nu/h\nu)$  without independent motivation for the discontinuity of heat radiation would surely appear to be an exercise in circularity or question begging, especially given that it entails a variability in the number of quanta.

So Einstein would not likely be tempted to try to use the ideal gas law as a signature for a discontinuous microstructure. If he had tried, what the disanalogies sketched in Section 5.3 indicate, however, is that he could not have used the analysis of his Brownian motion paper reviewed in Section 3.2 above without significant modification. The crucial disanalogy is that the analysis of Einstein's Brownian motion paper presumes a fixed number of components molecules or particles; it posits a phase space with a fixed number of coordinates and fixed dimension set by the number of components. The number of component quanta in heat radiation is variable and will change in processes that alter volume and temperature.

This is not to say that the gap is unbridgeable. There are techniques for extending the methods of Einstein's Brownian motion paper to thermal systems with a variable number of components. These were introduced by Gibbs with the transition from canonical ensembles, governed by the Boltzmann distribution (9), to grand canonical ensembles. The essential change is that the factor  $\exp(-E/kT)$  of the Boltzmann distribution is replaced by a more general factor that accommodates changes in the number of components in the thermal system:  $\exp[(\sum_i \mu_i n_i - E)/kT]$ . The quantities  $n_i$  are the number of components of the  $i$ th type in the system and  $\mu_i$  is their chemical potential, where  $\mu_i = (\partial E/\partial n_i)_{V,T}$ . This augmented theory can accommodate processes in which the numbers of components change, including processes that created new chemical species from others by chemical reactions. However the formalism of grand canonical ensembles cannot not be applied to quanta without some adjustment. Even in processes that create new chemical species, the changes are governed by the stoichiometry of the chemical process, which is expressed as constraint equations relating the changes in numbers of the different chemical species. In the case of energy quanta, these would have to be replaced by constraints that expressed the dependency of the number of quanta on the energy in each frequency range and the formalism correspondingly adjusted.

While Einstein's earlier work in statistical physics had independently developed along the lines of Gibb's approach, it did not contain notions corresponding to the grand canonical ensemble.

Finally, once we recognize that the variability of the number of quanta does present some sort of formal problem for Einstein's statistical techniques, we see that the particular process selected for the miraculous argument proves to be especially well chosen. Most thermal processes—including slow volume changes and heating—alter the number of quanta and thus require an extension of Einstein's statistical methods. In his miraculous argument, Einstein chose one of the rare processes in which the number of quanta remain fixed. In a random volume fluctuation, Einstein can arrive at expressions (14) and (15) exactly because the quanta interact with nothing and their number stays fixed. As a result, the analysis of this particular process is the same for both quanta and molecules.

### 5.5. Mean energy per quanta

These last considerations may also cast some light on a remark at the end of Section 6 of the light quantum paper. In modernized notation, Einstein wrote:

We also want to compare the mean value of the energy quanta of black-body radiation with the mean kinetic energy of the center-of-mass motion of a molecule at the same temperature. The latter is  $(3/2)kT$ , while the mean value of the energy quantum obtained on the basis of Wien's formula is

$$\int_0^\infty \frac{8\pi h\nu^3}{c^3} \exp\left(-\frac{h\nu}{kT}\right) d\nu \bigg/ \int_0^\infty \frac{1}{h\nu} \frac{8\pi h\nu^3}{c^3} \exp\left(-\frac{h\nu}{kT}\right) d\nu = 3kT.$$

The computation Einstein indicates is straightforward. The first integral is the energy per unit volume of full spectrum heat radiation according to Wien's distribution; the second is the total number of quanta per unit volume; and their quotient is the average energy per quantum.

That the mean kinetic energy of a molecule is  $(3/2)kT$  is the simplest application of the equipartition theorem. In slogan form, that theorem assigns  $(1/2)kT$  of mean energy to each degree of freedom of the component. A molecule has three degrees of freedom associated with its translational motion. Einstein had already used the theorem to good effect in this same paper in Section 1 in demonstrating the failure of Maxwell's electrodynamics to accommodate heat radiation. There he had expressed the theorem in terms of the kinetic energy of a gas molecule. For an electric resonator in thermal equilibrium, Einstein wrote, "the kinetic theory of gases asserts that the mean kinetic energy of a resonator electron must be equal to the mean translational kinetic energy of a gas molecules."

The juxtaposition of the mean energies of quanta and molecules in the passage quoted from Section 6 suggests that Einstein intended us to read the result in the context of the equipartition theorem. That is, energy quanta are systems with six degrees of freedom. So their mean energy is  $6 \times (1/2)kT = 3kT$ . Of course Einstein does not actually say that and, if we tease out just what this assertion says, we may understand why he would pause.

The slogan " $(1/2)kT$  per degree of freedom" is shorthand for a much more complicated result. The general result applies to systems that are canonically distributed according to (9). If the energy  $E$  of the system is a sum of monomials of the form  $b_i p_i^n$  for canonical phase space coordinates  $p_i$  and constants  $b_i$ , then each such term contributes a term  $(1/n)kT$  additively to the mean energy.<sup>22</sup> For a monatomic molecule of mass  $m$  with canonical momenta  $p_x$ ,  $p_y$  and  $p_z$ , the energy  $E = (1/2m)(p_x^2 + p_y^2 + p_z^2)$ . There are three monomials—three degrees of freedom—each with  $n = 2$ . Hence the mean energy is  $(3/2)kT$ .

So when a quantum has mean energy  $3kT$ , the natural reading is that it has six degrees of freedom. Three of them would be associated with the three translational degrees of freedom. The remaining three would be internal degrees of freedom, possibly associated with the quantum analog of the polarization of a classical light wave.

While this is the natural reading, it presumes a lot of theory. It presumes that there are six canonical coordinates, three of them linear momentum coordinates, and three others for the internal degrees of freedom. Moreover the energy is a sum of term quadratic in these six coordinates. To these six canonical coordinates, we must also add three canonical

<sup>22</sup>For the simple case of an energy  $E = bx^n$ , for  $b$  a constant and  $x$  a canonical coordinate, we have that the mean energy is  $\bar{E} = (1/Z) \int bx^n \exp(-bx^n/kT) dx$  where  $Z = \int \exp(-bx^n/kT) dx$  and the integrals extend over all values of  $x$ . Hence it follows that  $\bar{E} = -(1/Z)(\partial/\partial(1/kT)) \int \exp(-bx^n/kT) dx = -(\partial/\partial(1/kT)) \ln \int \exp(-bx^n/kT) dx$ . That is,  $\bar{E} = -(\partial/\partial(1/kT)) \ln[(kT^{1/n}) \int \exp(-bx^n/kT) d(x/kT^{1/n})] = kT/n$ . For this calculation in the case of  $n = 2$  see Einstein (1902, Section 6).



spatial coordinates that would not appear in the expression for the energy of the quantum. Finally, the Wien distribution, when re-expressed in appropriate terms should adopt the form of a Boltzmann distribution. That would mean that the canonical coordinates would need to relate to the parameter  $\nu$  such that the canonical volume element of the phase space in the degrees of freedom pertinent to energy would be<sup>23</sup>  $\nu^3 d\nu$ .

This is too much theory to be sustained merely by the result of a mean energy of  $3kT$ . For example, while we are used to energies that are quadratic in the canonical coordinates, nothing requires it. Since a term in  $bp_i^n$  yields a contribution of  $(1/n)kT$  to the mean energy, other combinations yield the same result. If the energy is linear in three canonical coordinates, we would recover the same mean energy, as we would if there were four canonical coordinates  $p_1, \dots, p_4$  and the energy of a quantum is  $E = h\nu = p_1^{4/3} + \dots + p_4^{4/3}$ .

Clearly finding the appropriate phase space structure is difficult problem. But perhaps it is a problem not even worth starting. Recall that the equipartition theorem is routinely developed in a statistical mechanical formalism that has a fixed number of components. One might assume that an extension of the formalism can be found that will accommodate a variable number of quanta, as suggested above. However surely that extension ought to be found and the correctness there of the equipartition theorem assured before trying to apply the theorem to quanta.

Finally we may wonder whether there is a simpler explanation for why Einstein introduced the remark about the mean energy of quanta. He may have been quite unconcerned with the issue of how many degrees of freedom are to be associated with the quantum and what their microscopic interpretation might be. A hallmark of the statistical physics of atoms, molecules and suspended particles is that their mean thermal energies are, to a very great degree, independent of their internal structures and sizes. Aside from a numerical factor, their mean energies are given by  $kT$ , even though a suspended particle may differ in size by orders of magnitude from an atom. Einstein may merely have wished to point out that quanta conform to this pattern and their mean thermal energies are largely independent of the details of their constitutions. The constant characteristic of quantum phenomena,  $h$ , does not appear in the formula for their mean energy, which Einstein wrote as  $3(R/N)T$ . The same constants  $R/N$  govern the mean energy of molecules and quanta.

## 6. Conclusion

What I hope to have established in this paper is that a single theme unifies Einstein's three statistical papers of 1905: his dissertation, Brownian motion paper and the light quantum paper. They all deal essentially with statistical systems of a particular type, those consisting of finitely many, spatially localized, independent components. They are the molecules of an ideal gas, solutes in dilute solution, particles suspended in liquid and the quanta of high-frequency radiation. The papers also develop the same idea, that this microscopic constitution is associated with definite macroscopic signatures. All of them conformed to the ideal gas law. In the dissertation and Brownian motion paper, this fact was exploited by Einstein as a convenient way of representing the average tendency of

<sup>23</sup>Under normal assumptions, this volume element  $\nu^3 d\nu$  is incompatible with an energy  $h\nu$  that is a quadratic sum of terms in six canonical coordinates, so that  $\nu$  is proportional to  $p_1^2 + p_2^2 + \dots + p_6^2$ . For in such a phase space, the volume element is  $p^5 dp$ , where  $p^2 = p_1^2 + p_2^2 + \dots + p_6^2$ . That is, the volume element is  $\nu^{5/2} d\nu$ .

components to scatter under their thermal motions; that tendency is the pressure of the ideal gas law.

While the quanta of high-frequency heat radiation conform to the ideal gas law as well, that signature of its components could not be used readily by Einstein to establish the existence of the quanta. One reason was that the variability of the number of quanta meant that Einstein's statistical analysis of the ideal gas law from his Brownian motion paper was inapplicable to quanta. Perhaps more significantly, the ideal gas law provides a secure signature for the independence of the components, but is a less secure indication of there being finitely many components and of their being spatially localized. In any case, Einstein found a better signature—the logarithmic dependence of the entropy of a single frequency cut of high-frequency radiation on volume—as a compelling way to establish that quanta lay behind the appearance of heat radiation. It enabled Einstein to argue for all the properties needed: that there are finitely many components, that they are spatially localized and that they are independent. This argument is so effective and its conclusion so startling that I have singled it out as worthy of the title of the miraculous argument among all the works of Einstein's miraculous year.

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### Appendix A. The ideal gas law

Sections 2.1 and 2.2 above sketched the “simple argument” that proceeds from the microscopic constitution of finitely many, spatially localized, independent components to the macroscopic property of the ideal gas law. It was also suggested that the inference can proceed in the reverse direction at least as far as we can infer the independence of the components from the ideal gas law. A more precise version of these inferences is developed here.

#### A.1. *Micro to macro*

The system consists of a large number  $n$  of components at thermal equilibrium at temperature  $T$  in a homogeneous gravitational field. According to the Boltzmann distribution, the probability density in the system's canonical phase space of any given configuration of components is determined by the total energy  $E_{\text{tot}}$  of the  $n$  components and is proportional to  $\exp(-E_{\text{tot}}/kT)$ . Under the presumption of independence, this total energy is given by the sum of the energies of the individual molecules  $E_{\text{tot}} = E_1 + \dots + E_n$ , since independence entails the absence of interaction energies. The energy  $E_i$  of each individual ( $i$ th) component is in turn determined by the component's speed and height  $h$  in the gravitational field  $E_i = E_{\text{KE}} + E(h)$  where  $E_{\text{KE}}$  is the kinetic energy of the component and  $E(h)$  is the energy of height for a component at height  $h$ . (That an inhomogeneous gravitational field can couple to a body through a single spatial position is a manifestation of the spatial localization of the body.) By convention, we set  $E(0) = 0$ . Since  $\exp(-(E_{\text{KE}} + E(h))/kT) = \exp(-E_{\text{KE}}/kT) \exp(-E(h)/kT)$  the kinetic energy of the

component will be probabilistically independent of the energy of height can be neglected in what follows.

Factoring the above exponential term from the Boltzmann distribution and integrating over the canonical momenta that fix the kinetic energy, we find that the probability density in space that a given component will be found at height  $h$  is

$$p(h) = \text{constant} \exp(-E(h)/kT). \tag{22}$$

Since the position of the components are independent of one another, the spatial density  $\rho(h)$  of components at height  $h$  is proportional to the probability  $p(h)$ . The inferences now proceed as in Section 2.1.

### *A.2. Macro to micro*

The reverse inference to the independence of the components is more difficult to achieve. Assuming that there are finitely many, spatially localized components, it is possible, in so far as it can be shown that satisfaction of the ideal gas law precludes an interactions between the components that is a function of the spatial positions and the distance between components. The ideal gas law does not preclude coupling of the components via their canonical momenta.<sup>24</sup> However, such coupling is not normally considered in the classical context since such interactions are not weakened by distance.

The inference proceeds most easily for Einstein’s 1905 derivation of the ideal gas law in his Brownian motion paper, reviewed in Section 3.2 and yields the absence of short range interaction forces. To invert the inference we begin with the ideal gas law  $PV = nkT$  for a homogeneous system of  $n$  components occupying a volume  $V$  of space. We relate the pressure  $P$  to the free energy  $F$  via thermodynamic relation (10):

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{nkT}{V}.$$

Integrating, we have that

$$F = -nkT(\ln V) + \text{constant}(T).$$

From (6) we have that

$$F = -kT \ln \int \exp(-E/kT) d\pi dx$$

for a canonically distributed system with canonical coordinates  $x$  and  $\pi$  as described in Section 3.2, where  $dx_1 dy_1 dz_1 \dots dx_n dy_n dz_n$ . It follows that

$$\int \exp(-E/kT) d\pi dx = V^n \text{constant}(T). \tag{23}$$

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<sup>24</sup>The easiest way to see that such coupling is not precluded is to note that the corresponding interaction energies would appear in the term  $J$  of Eq. (8) of Einstein’s derivation of the ideal gas law and their presence would not affect the recovery of the ideal gas law when the partial differentiation of (10) is carried out. Analogously, these interaction energies would not affect the simple argument of Section 2.1 and the Appendix since they would be absorbed into the constant of Eq. (22) formed by integration over the canonical momenta.

Now consider a system extending over a very small spatial volume  $\Delta V$  for which  $\Delta V \approx dx_i dy_i dz_i$ . The above integral becomes, to arbitrarily good approximation

$$(\Delta V)^n \int \exp(-E/kT) d\pi = (\Delta V)^n \text{constant}(T).$$

It now follows that the energy  $E$  of the  $n$  components in the volume  $\Delta V$  is independent of their spatial coordinates. This precludes any interaction energies that are functions of distance within the short ranges confined to the small volume  $\Delta V$ . I expect that a more careful examination of (23) would yield the absence of longer-range interactions.

The absence of such longer-range interactions can be recovered from an inversion of the simple argument of Section 2.1 if we presume that these longer-range interactions do not depend upon the orientation in space of the interacting components. To invert the simple argument, we start with the ideal gas law  $P = \rho kT$  for a system of many components in a gravitational field. To determine the gravitational force density on the components, we take the state of the system at just one instant and consider the energy of a component at height  $h$ . Its energy will be given by some expression  $E(h, x_{\text{eq}})$  where the vector quantity  $x_{\text{eq}}$  represents the positions of all  $n$  components of the system at that moment in the equilibrium distribution, excluding the height component of the position of the component in question. The presence of this quantity  $x_{\text{eq}}$  as an argument for  $E$  represents the possibility that the energy of the component may also depend on the positions of the remaining components; that is, that the component is not independent of the others.

Differentiating the ideal gas law, we recover:

$$\frac{dP}{dh} = kT \frac{d\rho(h)}{dh}.$$

The gravitational force density  $f$  at height  $h$  at that instant is given

$$f = -\frac{dE(h, x_{\text{eq}})}{dh} \rho(h) = \frac{dP}{dh},$$

where the second equality is the condition that the gravitational force density is equilibrated by a gradient in the pressure  $P$ . Combining the last three equalities, we have

$$\frac{d\rho(h)}{dh} = -\frac{1}{kT} \frac{dE(h, x_{\text{eq}})}{dh} \rho(h).$$

The solution of this differential equation is

$$\rho(h) = \rho(0) \exp(-E(h, x_{\text{eq}})/kT), \quad (24)$$

where by convention  $E(0, x_{\text{eq}}) = 0$ .

To see that there are no interaction terms of low order in the number of components, consider the density of clusters of  $m$  components at the same height  $h$ , where  $m$  is much smaller than  $n$ . Since the clusters are only required to be at height  $h$ , the components forming the clusters may be well separated in space horizontally. Presuming that the system is homogeneous in the horizontal direction, the ideal gas law, re-expressed in terms of the density  $\rho_m = \rho/m$  of clusters of size  $m$  is  $P = \rho_m m kT$ . Repeating the derivation above, we find that the density at height  $h$  of these  $m$ -clusters is

$$\rho_m(h) = \rho_m(0) \exp(-E_m(h, x_{\text{eq}})/mkT),$$

where  $E_m(h, x_{\text{eq}})$  is the energy of each  $m$ -cluster of components at this same instant in the equilibrium distribution. Recalling that  $\rho_m = \rho/m$ , we now have

$$\rho(h) = \rho(0) \exp(-E_m(h, x_{\text{eq}})/mkT).$$

Comparing this expression for  $\rho(h)$  with (24), we infer  $E_m(h, x_{\text{eq}}) = mE(h, x_{\text{eq}})$ . That is, the energy of a cluster of  $m$  components at height  $h$  is just  $m$  times the energy of one component at height  $h$ , which asserts the independence of the energy of each component in the cluster from the others. Since the components in the cluster may be widely spaced horizontally and the law of interaction by presumption does not distinguish horizontal and vertical directions, it follows that there is no interaction, either short or long range, for  $m$  components.

Thus we preclude any interaction between the components up to  $m$ -fold interactions. That leaves the possibility of interactions that only activate when more than  $m$  components are present. We can preclude any such higher-order interaction being activated and relevant to the equilibrium distribution if we assume that all interactions are short range, for the above argument allows us to set  $m$  at least equal to the number of component that can cluster together in one small location over which a short range interaction can prevail.<sup>25</sup>

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<sup>25</sup>The theory of virial coefficients (Eyring et al., 1982, Ch. 11) gives a more systematic treatment of the orders of interaction. In that theory, the ideal gas law  $P = \rho kT$  is generated from a Hamiltonian that has no terms representing interactions between the components. Adding interaction terms augments the  $\rho$  dependence of pressure to  $P = \rho kT(1 + B(T)\rho + C(T)\rho^2 + \dots)$ , where the second, third, ... virial coefficients  $B(T)$ ,  $C(T)$ , ... arise from adding terms to the Hamiltonian that represent pairwise component interactions (for  $B(T)$ ), three-way component interactions (for  $C(T)$ ), and so on. Since the  $n$ th virial coefficient appears only if there is an  $n$ -fold interaction, the reversed macro to micro inference is automatic, under the usual assumptions of the theory. (Notably, they include that the interaction terms are functions of the differences of molecular positions only.) Since the second, third and all higher order virial coefficients vanish for the ideal gas law, we infer from the law that the gases governed by it have non-interacting molecules. (I am grateful to George Smith for drawing my attention to the virial coefficients.)

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